

Use of Models for Phosphorus Adsorption on Some Sodic Soils of Punjab

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ABSTRACT

Langmuir, Freundlich, two surface Langmuir and Linear adsorption model were applied on seven different textured sodic soils varying in their P adsorption capacity, in order to characterize the P adsorption isotherms for these sodic soils. Langmuir and Freundlich models proved equally good for these sodic soils based on correlation coefficient values. In soil 1, 2, and 3 Langmuir models showed its superiority over the Freundlich model. While in soil 4, 6, and 7, Freundlich model proved better. However, in soil 5 both the Langmuir and Freundlich model came at par with each other. Langmuir models showed two straight lines in each soil. Two surface Langmuir model proved better in the region II (average $r = 0.7268$), while in region I (average $r = 0.6900$) results were non-significant except soil 4 and 5 with r -values 0.9270^{**} and 1.000^{**} . Bonding energy constants calculated by two surface Langmuir model were high in region I while low in the region II and vice versa. It means that a small amount of P in region I held firmly while a slightly greater amount of P held less firmly in region II. This indicated that two group of sites exists in these sodic soils. One group was got activated at lower P concentration while other group became active at slightly higher P concentration. A parallel relationship between the pH of the equilibrium P solution (EPS) and % adsorption was noted. This indicated an inverse relationship between pH and soil P saturation. Similarly, an inverse relationship was inferred between soil P saturation and % adsorption of P. It was observed that with increasing P saturation of the soil components, OH⁻ may be released. Langmuir and Freundlich adsorption parameters (K_L , b , K_f , and $1/n$) significantly correlated with sand, silt and organic matter percent contents. These soil properties may be responsible for P adsorption in these sodic soils. Freundlich K_f significantly correlated with Langmuir adsorption maximum (b) value (0.898^*), which may made possible for one to be able to calculate adsorption maximum value where Langmuir model got failed to justify itself like in soil 6 in this study.

Key Words: Langmuir; Freundlich; Adsorption Isotherms; pH; Sodic soils

INTRODUCTION

In commonly used form of the Langmuir adsorption model, a straight line is believed to obtain when equilibrium concentration divided by the amount of adsorption per unit adsorbent is plotted against equilibrium P concentration of adsorbate. Similar results are expected in the Freundlich model when $\log(x/m)$ is plotted vs. $\log C$ (Hussain *et al.*, 2003). Generally, the comparisons among these models are based on the goodness of fit, but fitness is over a limited range of P concentration. This problem has been resolved by adding square root term to the equation (Gunary, 1970), by assuming that theory is obeyed only at low equilibrium P concentration, by portioning the curve into two straight lines referring as region I and II (Syers *et al.*, 1973; Rajan & Watkinson, 1976), and/or application of Freundlich model (Polyzopoulos *et al.*, 1985). Muljadi *et al.* (1966) described adsorption reactions that may be responsible for different slopes (i) adsorption at various sites on the surface; (ii) adsorption occurring in layer on the surface; (iii) adsorption of mineral species being nucleated on the surface. Bache and Williams (1971) suggested that the deviation were due to sorbed P migration into the surface layer. Harter and Baker (1977) suggested a multiple adsorption mechanism and pointed out that the effect of desorbed ions in the

equilibrium solution is neglected in the usual form of the Langmuir model. Freundlich model is considered to be pragmatic in nature but has been used extensively to describe the adsorption of phosphate by soils (Hussain *et al.*, 2003; Gregory *et al.*, 2005). Syers and Curtin (1989) stated that adsorption-desorption is the dominant inorganic process influencing soil solution P concentration. Understanding of P adsorption and desorption by soils is important for fertilizer management. Little is known about the P sorption characteristics of calcareous soils (Zhou & Li, 2001) as well as of sodic soils. The adsorption of P in soils occurred at relatively low P concentration which is indicated by small Freundlich K_f values (Low Freundlich K_f values indicate low P adsorption at lower P concentration). While at high solution P concentration, precipitation occurred (Zhou & Li, 2001). Dominguez *et al.* (2001) concluded that the ratio of Ca phosphate precipitation to P adsorption might be higher compared to soils high in Na saturation. Adsorption of P by sodic soils decreased sharply as the pH increases (Barrow, 1984; Curtin *et al.*, 1992b). Increasing sodicity also tends to change the equilibrium between adsorbed (extractable-P in 0.5 M NaHCO₃) and solution-P (water extractable-P) in favor of the latter (Curtin & Naidu, 1998). Curtin *et al.*, (1992a) demonstrated that relatively small amount of exchangeable Na could have a significant effect on P

solubility. Exchangeable Na enhances the dissociation of organic anions, which exchange phosphate anions from Al and Fe complexes and thus increase the concentration of soluble P (Naidu & Rengasamy, 1993). Several researchers have reported positive relationships between the organic matter contents of soils and P sorption (Owusu-Bennoah & Acquaye, 1989; Sanyal De Datta, 1991; Singh & Gilkes, 1991). The role of organic matter in increasing the ability of soils to sorb P has been attributed to its association with cations such as Fe, Al and Ca (Singh & Gilkes, 1991).

The objectives of study are to 1) characterize the P adsorption models for different sodic soils, 2) demarcate between adsorption and precipitation processes based on Freundlich K_f values, 3) determine soil properties responsible for P adsorption by correlation techniques and 4) study the changes in pH behavior occurred during adsorption/precipitation process.

MATERIALS AND METHODS

Seven sodic soil samples (Table I) were collected from different sites of the Faisalabad district. After air-drying soils were ground with wooden mortar and pestle and passed through 2 mm sieve. Saturated soil pH was measured by Jenco digital pH meter (model 671P); EC_e by Jenway EC meter (model 4070); soluble CO_3 , HCO_3 , Cl, and Ca+Mg by titration methods (Page *et al.*, 1982); Na and K by Jenway PFP-7 flame photometer; exchangeable Na and K by CH_3COONH_4 extraction method; CEC by CH_3COONa saturation and organic matter by Walkley-Black procedure (Nelson & Sommer, 1986), lime by Calcimeter (Moodie *et al.*, 1959) and particle size analysis by hydrometer method after dispersing soil in sodium hexametaphosphate (Bouyoucos, 1962). In 0.01 M $CaCl_2$ solution different P concentration (0, 0.38, 0.73, 1.6, 3.7, 7.6, 15.79, 26.70, 55.91, 86.44 mg P L^{-1}) using KH_2PO_4 were developed. Three grams of each soil sample were placed in 30 mL of each solution P concentration overnight at 25 ± 2 °C. The soil-P solution suspensions were centrifuged and P in supernatant solution was determined colorimetrically at 882 nm wavelength (Watanabe & Olsen, 1965). The difference between the amount of P added and in supernatant solution was taken as P adsorbed/precipitated. The amounts of P adsorbed/precipitated converted from mg P L^{-1} to mg kg^{-1} by using the formula (John, 2000) as:

$$x/m = [C_0 - C] \times V \div W_s \quad \text{Where,}$$

x/m is adsorption/precipitation of P at equilibrium (mg P kg^{-1})
 C_0 is the initial concentration of P added (mg P L^{-1})
 C is the concentration of P in solution after 24-h equilibrium (mg P L^{-1})
 V is the volume of P solution added (L)
 W_s is the oven dry weight of soil (kg)

The experiment was run in triplicate, means of which were used for further calculations. The data so collected were computed according to the Linear, Langmuir, Freundlich and two surface Langmuir models. pH of the equilibrium solutions (EPS) were noted for correlating with the experimental P-adsorption values. The Langmuir and

the Freundlich adsorption parameters were correlated with different soil properties and among themselves.

1. Linear Model: $x/m = A + B(C)$
2. Langmuir Model: $x/m = [K_L b(C) / (1 + K_L C)]$
3. Two surface Langmuir Model: $x/m = [(K_{Ib}C) / (1 + K_I C) + (K_{IIb}C) / (1 + K_{II} C)]$
4. Freundlich Model: $x/m = K_f C^{(1/n)}$

Where,

- C = Concentration of P in soil solution at equilibrium (EPC) (mg L^{-1})
 x/m = Amount of P adsorbed/precipitated (mg P kg^{-1} soil)
 $1/b$ = Slope of the line, when $[C/(x/m)]$ vs. C was plotted
 b = Adsorption maximum (mg P kg^{-1} soil) = reciprocal of the slope
 $1/K_L b$ = Y-intercept of the Langmuir model, when $[C/(x/m)]$ vs. C was plotted
 $K_L b$ = Reciprocal of Y-intercept
 K_L = Bonding energy constant ($L \text{ mg}^{-1} P$) = $K_L b / b$
 K_f = Proportionality constant for the Freundlich model (mg kg^{-1}), i.e. extent of adsorption (Bahl & Toor, 2002) = Antilog (Y-intercept)
 $1/n$ = Slope of the curve, when $\log(x/m)$ vs. $\log(C)$ was plotted
 A = Y-intercept, when x/m vs. C was plotted (mg kg^{-1}), i.e. Native originally adsorbed P, having negative sign (Graetz & Nair, 1995)
 B = Slope of line, when x/m vs. C was plotted. Slope is the buffering capacity of soils with respect to P and clay contents

Subscript I and II with K and b symbolize the region of straight line corresponding to the relatively low and high equilibrium P concentration, respectively.

RESULTS AND DISCUSSION

Soils used in this study differed widely in their P adsorption capacity (Fig. 1). Main objective of adsorption isotherms is to obtain a straight-line graph. Therefore, linear adsorption, Langmuir, two surface Langmuir, and Freundlich models were tested on these seven sodic soils. The soils under test were sodic with pH 8.36 to 9.59, SAR 13.06 to 26.55 and have different textures (Table I).

Langmuir Model. Adsorption of P by the soils (Fig. 2) conformed to Langmuir isotherm better than the linear model in all the soils except soil 6 and 7 (Table IV). The values of adsorption maximum (b) and bonding energy constant (K_L) are given in Table II which are ranged from 109.89 to 344.83 mg P kg^{-1} soil and 0.064 to 0.98 $L \text{ mg}^{-1}$, respectively. Kumar and Singh (1998) reported that Langmuir constants of adsorption maximum and bonding energy ranged from 110.2 to 142.2 mg P kg^{-1} soil and 0.43 to 1.31 $L \text{ mg}^{-1}$, respectively. Langmuir model showed two straight lines. The deviation of the isotherm may be either due to precipitation (Zhou & Li, 2001). In soil 6, Langmuir isotherm showed negative relationship but non-significant with irregular trends. Similarly Singh *et al.* (1991) reported a negative relationship for the Kanpur soil. Irregular trends of curve in soil 6 may be due to the heterogeneous nucleation (Griffin & Jurinak, 1973) of calcium phosphate on the surface of $CaCO_3$ or precipitation of Phosphates (Castro & Torrent, 1998). Zhou and Li (2001) reported that precipitation on the

Table I. Physico-chemical properties of soils used for adsorption studies

Soil properties	Soil sample No.						
	1	2	3	4	5	6	7
pH _e	8.69	8.27	9.07	8.36	8.41	8.79	9.59
EC (dS m ⁻¹)	3.67	2.74	2.05	3.82	3.13	2.44	3.76
TSS (mmol _e L ⁻¹)	40	29	22	42	34	25	41
SAR	21.7	16.64	19.23	17.55	14.29	13.06	26.55
ESP	40.93	23.09	34.73	22.69	20.98	34.37	56.56
Soil Type	Sodic	Sodic	Sodic	Sodic	Sodic	Sodic	Sodic
CEC (cmol _e kg ⁻¹)	6.67	18.78	8.35	5.95	6.33	4.83	6.1
Olsen-P (mg kg ⁻¹)	16.56	32.29	21.18	22.41	15.13	21.19	17.92
Soluble cations (mmol_e L⁻¹)							
Na ⁺	33	24.13	20	33.69	26.45	20.5	36.37
K ⁺	1.29	0.56	0.51	0.9	1.16	0.53	0.487
Ca ²⁺	2.13	1.93	0.93	3.67	3.4	2.87	1.8
Mg ²⁺	2.47	2.27	1.27	3.66	3.47	2.06	1.93
Soluble anions (mmol_e L⁻¹)							
HCO ₃ ⁻	7.2	10.9	7.37	14.6	8.06	7.33	10.87
Cl ⁻	25.46	10.37	7.33	18.65	19.75	16.83	11.02
SO ₄ ²⁻	7.34	7.73	7.3	8.75	6.19	0.84	17.11
Exchangeable cations (mmol_e kg⁻¹)							
Na ⁺	2.73	4.34	2.9	1.35	1.33	1.66	3.45
K ⁺	0.37	0.52	0.65	0.21	0.22	0.19	0.23
Ca ²⁺ +Mg ²⁺	3.57	13.92	4.8	4.39	4.78	2.98	2.42
%age							
Saturation	26.91	44.08	32.24	28.91	25.69	31.97	38.34
CaCO ₃	1.12	0.57	4.31	1.44	2.89	4.87	4.36
OM	1.15	0.17	0.18	0.16	0.2	0.28	0.19
Clay	17.32	51.9	31.2	16.6	13.72	18.11	27.5
Silt	23	28.95	44.61	21.95	19.6	63.3	58.13
Sand	59.58	19.15	24.19	61.45	66.68	18.59	14.37
Textural class	Sandy loam	Clay	Clay loam	Sandy loam	Sandy loam	Silt loam	Silty clay loam

Table II. Adsorption parameters of the Langmuir and the Freundlich models for sodic soils

Soil #	Langmuir parameters					Freundlich parameters			SEPC
	Slope = (1/b)	b (mg kg ⁻¹)	Y-intercept = (1/K ₁ b)	K ₁ b (mg kg ⁻¹)	K ₁ (L mg ⁻¹) = (K ₁ b/b)	Y-intercept = (log K _f)	K _f (mg kg ⁻¹)	Slope = (1/n)	
1	0.0072	138.8889	0.0075	132.9787	0.9574	1.0008	10.0200	0.7188	1.94
2	0.0057	175.4386	0.0383	26.1097	0.1488	1.2565	18.0500	0.6585	3.96
3	0.0063	158.7300	0.0438	22.8310	0.1438	1.2165	16.4600	0.7334	3.04
4	0.0097	103.0928	0.1127	08.8731	0.0860	0.8663	07.3500	0.6770	1.54
5	0.0091	109.8901	0.0605	16.5289	0.1504	1.0940	12.4200	0.5750	3.30
6	0.0029	344.8276	0.0453	22.0751	0.0640	1.4675	29.3400	0.9752	3.10
7	0.0042	238.0900	0.0202	49.5049	0.2079	1.4840	30.4790	0.7878	4.97

carbonate surface is likely the dominant process at high P concentrations. For most of the soils, the adsorption isotherm could be divided into two regions, which also suggest the affinity of P for at least two energetically different reaction sites.

Two Surface Langmuir Model. In most of the soils, the adsorption isotherm could be divided into two regions. Therefore, two surface Langmuir model was tested as suggested by Syers *et al.* (1973). Phosphorus sorption data plotted according to the two surface Langmuir model indicated that straight-line relationship did not exist over the entire initial P concentration of 0.38 to 86.44 mg L⁻¹. Therefore, the curves were partitioned into two linear portions and referred as region I and region II respectively for low and high P concentrations at equilibrium. In each region, C/(x/m) vs. C was plotted and values of adsorption maximum (b_I and b_{II}) and bonding energy constant (K_I and K_{II}) were calculated separately (Table III) for each soil and graph region. Adsorption maximum values (b_{II}) were higher in region II and bonding energy constant values were lower in this region and vice versa (Fig. 3). These finding

indicated that soil adsorbed a small amount of P firmly and slightly greater amount of P less firmly and so on. Two surface Langmuir model (Table V) showed that region I sites were more important for their higher bonding energies and region II sites were important for their higher adsorption affinities. However, soil 1, 2, 3, 6 and 7 data did not permit to calculate two surfaces Langmuir model at a significant r-value. According to the correlation coefficient value, two surface Langmuir model did not prove good in region I (average r = 0.6900). This might be due to very low EPC. Zhou and Li (2001) reported deviation on very low EPC due to too low P concentration to be determined. This might be due to heterogeneous nucleation of calcium phosphate on the surface of CaCO₃ (Griffin & Jurinak, 1973).

Freundlich Model. From the data plotted according to the linear form of the Freundlich model, almost an analogous linear relationship was observed. Values of the exponent (1/n) were less than one in all the models (Table IV). Similar results were reported by Fitter and Sutton (1975). Freundlich model is empirical in nature and implies that sorption decreases exponentially with increasing saturation

Table III. Region wise Langmuir adsorption parameters for sodic soils

Region I					
Soil #	slope _I =(1/b)	b _I (mg kg ⁻¹)	Y-intercept _I =(1/ K _I b _I)	K _I b _I (mg kg ⁻¹)	K _I (L mg ⁻¹) = K _I b _I / b _I
1	0.0253	18.868	0.0578	17.300	0.9169
2	0.008	125.0	0.0344	29.069	0.2325
3	0.156	64.103	0.0254	39.370	0.6142
4	0.0227	44.053	0.0855	11.695	0.2655
5	0.0242	41.322	0.0263	38.023	0.9200
6	0.0335	29.850	0.0324	30.864	1.034
7	0.0008	125.00	0.0248	40.32	0.32
Region II					
Soil #	slope _{II} =(1/b)	b _{II} (mg kg ⁻¹)	Y-intercept _{II} =(1/ K _{II} b _{II})	K _{II} b _{II} (mg kg ⁻¹)	K _{II} (L mg ⁻¹) = K _{II} b _{II} /b _{II}
1	0.0067	149.254	0.0948	10.548	0.0707
2	0.0051	196.078	0.0581	17.211	0.0877
3	0.0076	131.579	0.0387	25.839	0.1964
4	.0086	116.279	0.1615	6.192	0.0532
5	0.0087	114.942	0.0791	12.642	0.1099
6	-0.0081	-123.457	0.0635	15.748	-0.01276
7	0.0046	217.39	0.0117	85.47	0.393

Table IV. Freundlich, Langmuir and Linear adsorption type equations for sodic soils

Soil	Freundlich model	Correlation coefficient (r)	Langmuir type model	Correlation coefficient (r)	Linear adsorption model	Correlation coefficient (r)
1	x	0.9840**	x (132.979) C	0.9900**	x	0.9390**
	--- = 10.02 C ^{0.7188}		--- = -----		--- = 13.994 + 2.322 (C)	
2	m	0.9030**	m 1 + 0.9575 C	0.9720**	m	0.8420**
	x		x (26.1097) C		--- = 18.093 + 3.887 (C)	
3	m	0.9740**	m 1 + 0.1488 C	0.9880**	m	0.8360**
	x		x (22.830) C		--- = 11.820 + 5.739 (C)	
4	m	0.9900**	m 1 + 0.1438 C	0.9740**	m	0.9450**
	x		x (08.8731) C		--- = 10.635 + 1.515 (C)	
5	m	0.9800**	m 1 + 0.0861 C	0.9810**	m	0.8980**
	x		x (16.5289) C		--- = 15.896 + 1.761 (C)	
6	m	0.9450**	m 1 + 0.1504 C	-0.1980 ^{NS}	m	0.9070**
	x		x (22.0751) C		--- = -12.928 + 48.174 (C)	
7	m	0.9610**	m 1 + 0.0640 C	0.8860**	m	0.9900**
	x		x (49.5049) C		--- = 27.776 + 7.258 (C)	
Aver.		0.9624	m 1 + 0.2079 C	0.8555		0.9210

**= Correlation is significant at the 0.01 level (2-tailed); *= Correlation is significant at the 0.05 level (2-tailed); NS= Non-significant; r values between - 0.1980 to 0.9900 and n = 9

of exchange sites with P. Kuo and Lotse (1974) stated that one of the interesting characteristic of the exponent was its time independence (same slope after 1 and 24 hour) and that value of the exponent had generally been found less than one. Slope of the Freundlich model (1/n) is a measure of the heterogeneity of a system. A more homogeneous system will have (1/n) value approaching unity and a more heterogeneous system will have 1/n value approaching zero (Gregory *et al.*, 2005). It is obvious from the Table II that soil 5 have minimum (1/n) value, i.e. 0.5750 while soil 6 have maximum (1/n) value, i.e. 0.9752 approaching unity. Therefore, soil 6 will be more homogeneous while soil 5 will be more heterogeneous. It was also observed that 1/n was positively and significantly correlated (Table VI) with percent silt (r = 0.866**).

A significant positive correlation between K_f and Y-intercept of linear adsorption model was observed [r = 0.911**, Y-intercept = 0.6883(K_f) + 5.4963]. When the

Freundlich K_f was divided by a value taking the antilog of the Freundlich slope [K_f/ antilog (1/n) = SEPC], solution P concentration equilibrium (SEPC) with adsorbed P was calculated. These values were indicated in Table II. Bowman (1982) stated that K_f is the amount of sorbed P that would sustain a unit P concentration in equilibrium solution. Kuo and Lotse (1974) described that K_f is dependent on the solution concentration. Zhou and Li (2001) called it adsorption capacity while according to Bahl and Toor (2002) it is extent of adsorption (mg kg⁻¹). Zhou and Li (2002) stated that low Freundlich K_f values indicate low P adsorption capacities at low P concentrations (≤ 1 mg P L⁻¹). Moreover, even a large amount of P may be retained by precipitation at high P concentration.

Comparisons of the models. Generally, the choice among models is often based on the goodness of fit (Polyzopoulos, 1985). It is clear from Table IV that Freundlich model proved better over both the Langmuir model and linear

Fig. 1. Adsorption isotherms for sodic soils under investigation

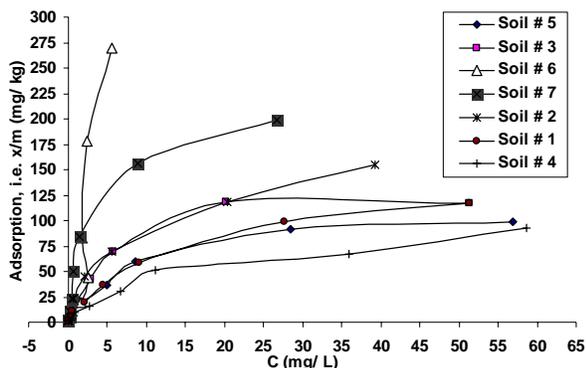
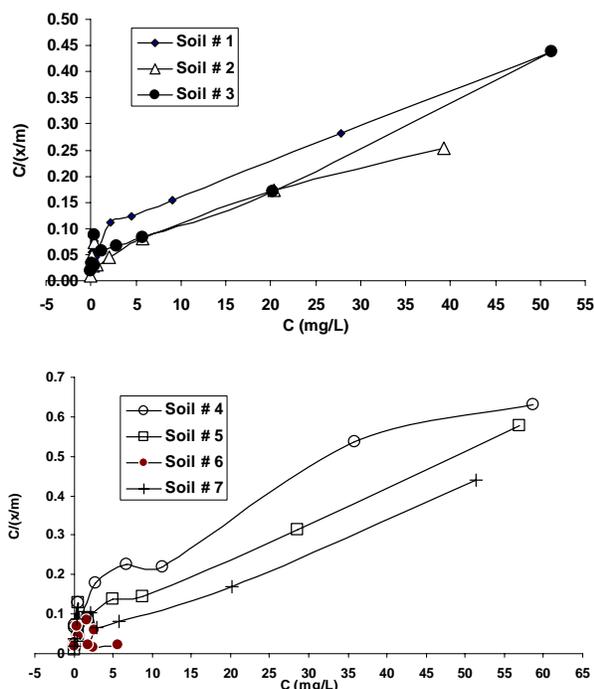
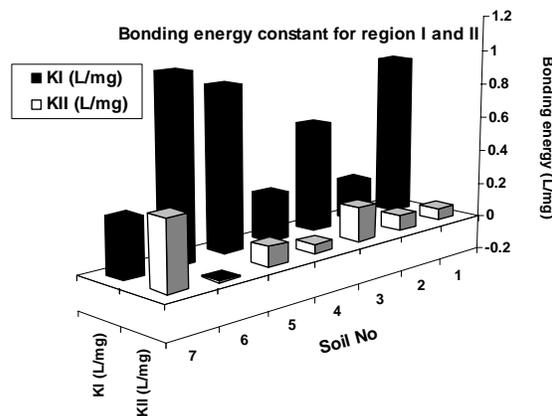
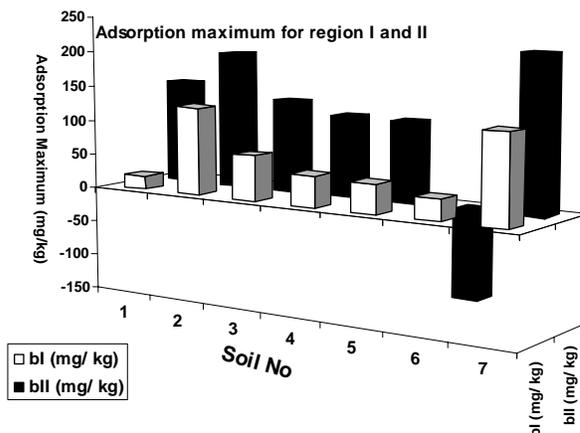


Fig. 2. Langmuir isotherms for sodic soils under investigation



adsorption model based on average correlation coefficient values (r) in all the soils under investigation. On individual soil basis, the Langmuir model and Freundlich model proved themselves equally good. In soil 1, 2 and 3 Langmuir model showed superiority over the Freundlich model [(average $r = 0.9833$ (Langmuir) > 0.9537 (Freundlich)]. Polyzopoulos *et al.* (1985) and Del Bubba *et al.* (2003) reported better results of the Langmuir model than the Freundlich model during the P adsorption studies. In soil 4, 6 and 7 Freundlich model proved good on the basis of correlation coefficient values [(average $r = 0.9653$ (Freundlich) > 0.6863 (Langmuir)]. Bakheit and Pakermanjie (1993) and Gregory *et al.* (2005) found that ability of the Freundlich model to describe P adsorption

Fig. 3. Comparison of adsorption maximum and bonding energy constants



curves was superior to the Langmuir model for calcareous soils. In soil 5 both the Langmuir and the Freundlich model remained at par with respect to correlation coefficient values of 0.9810^{**} and 0.9800^{**} respectively. Langmuir model in soil 6 completely failed to describe adsorption data. In case of two surface Langmuir model, model fit better in the region II [average $r = 0.7268$ (region II) > 0.6900 (region I)] as compare with region I based on correlation coefficient values (Table V). Model proved better in soil 1, 2, 3 and 7 in region II over the Freundlich and single surface Langmuir model [average $r = 0.9977$ (region II) > 0.9590 (Langmuir) > 0.9555 (Freundlich)].

Correlation between adsorption parameters.

Relationship between Langmuir adsorption parameters, [i.e. adsorption maximum (b), and bonding energy constant (K_L)] and Freundlich adsorption parameters (K_f and $1/n$) are presented in Table VI. Significant correlations were observed between $1/n$ vs. b (0.9210^{**}), K_f vs. b (0.8980^{**}). These results showed that Langmuir adsorption maximum (b), Freundlich (K_f) and ($1/n$) have some relationships. With the help of this relationship, one can be able to calculate the value of adsorption maximum from the Freundlich model. If the Freundlich model showed

Table V. Two surface Langmuir type equations for sodic soils

Soil #.	Langmuir type equations for region I	Correlation coefficient (r)	Coefficient of determination (R ²)	Langmuir type equations for region II	Correlation coefficient (r)	Coefficient of determination (R ²)	Two surface Langmuir type equations
1	x (17.30) C	0.7490 ^{NS}	0.7566	x (10.55) C	1.0000**	0.9998	x (17.30) C (10.55) C
	m 1+ 0.9169 C			m 1+ 0.0707 C			m 1+ 0.9169 C 1+ 0.0707 C
2	x (29.07) C	0.6430 ^{NS}	0.4137	x (17.21) C	0.9950**	0.9896	x (29.07) C (17.21) C
	m 1+ 0.2325 C			m 1+ 0.0877 C			m 1+ 0.2325 C 1+ 0.0877 C
3	x (39.37) C	0.6880 ^{NS}	0.1435	x (25.84) C	0.9970**	0.9933	x (39.37) C (25.84) C
	m 1+ 0.6162 C			m 1+ 0.1964 C			m 1+ 0.6162 C 1+ 0.1964 C
4	x (11.69) C	0.9270**	0.8587	x (6.192) C	0.9730**	0.9461	x (11.69) C (6.192) C
	m 1+ 0.2655 C			m 1+ 0.0532 C			m 1+ 0.2655 C 1+ 0.0532 C
5	x (38.03) C	1.000**	0.9195	x (12.64) C	0.7040 ^{NS}	0.9958	x (38.03) C (12.64) C
	m 1+ 0.9200 C			m 1+ 0.1099 C			m 1+ 0.9200 C 1+ 0.1099 C
6	x (30.86) C	0.8180 ^{NS}	0.6699	x (15.75) C	0.4170 ^{NS}	0.1741	x (30.86) C (15.75) C
	m 1+ 1.034 C			m 1+ (-0.128) C			m 1+ 1.034 C 1+ (-0.128) C
7	x (40.32) C	0.0200 ^{NS}	0.0060	x (85.47) C	0.9990**	0.9978	x (40.32) C (85.47) C
	m 1+ 0.32 C			m 1+ (0.343) C			m 1+ 0.32 C 1+ (0.343) C
Aver.		0.6900	0.5382		0.7268	0.8669	

**= Correlation is significant at the 0.01 level (2-tailed); * = Correlation is significant at the 0.05 level (2-tailed); NS= Non-significant; r values between 0.02 to 1.00 and n = 9

superiority over the Langmuir model as is the case with soil 6. It is impossible to calculate adsorption maximum directly from the Freundlich model. Similarly, the adsorption maximum (b) which is the reciprocal of the slope of the Langmuir model, is interrelated with the slope of the Freundlich model.

Relationship between pH and P adsorption. When % adsorption [(P adsorbed / Initial P added) × 100] was plotted against log (x/m) and pH of the equilibrium P solution (EPS). It was noted that pH and log (x/m) curves were the images of each others and run in opposite direction. pH curves gave constantly positive slopes while log (x/m) curves conferred always negative slope excluding that for soil 1, in which both curves showed same pattern, i.e. negative slopes. At low initial P addition (3.8 mg kg⁻¹), % P adsorption was maximum while at high initial P addition (864.4 mg kg⁻¹), % P adsorption was minimum. At low initial P addition (3.8 mg kg⁻¹), pH of the EPS was minimum while at high initial P addition (864.4 mg kg⁻¹) pH of the EPS was maximum. As the adsorption increased, % adsorption decreased with each increment of P addition. It can be concluded that soils P saturation increased as the adsorption increased, but % adsorption decreased, i.e. soil P saturation was increased. At maximum soil P saturation, pH of EPS was minimal while at minimum soil P saturation, pH was maximal, i.e. inverse relationship existed between pH and soil P saturation. A parallel relationship between the pH of the EPS and % adsorption was noted, i.e. as % adsorption increased, pH of EPS was also increased and vice versa. Similarly, an inverse relationship between soil P saturation and % adsorption was noticed.

Ryden *et al.* (1977) reported a change in pH during sorption in region I. In region II, pH increased rapidly to a

value of approximately 7 at a point b, where region II approached saturation. Only a very small increase in pH occurred during sorption in region III. They suggested that OH⁻ is released only during sorption in region II. Ioannou *et al.* (1994) described that adsorption increased linearly with decreasing pH.

Phosphorus adsorption and precipitation. Freundlich K_f is antilog of Y-intercept, when log (x/m) vs. log C was plotted. By taking the antilog of Y-intercept, it was converted to P adsorbed (mg P kg⁻¹). It is the value of P adsorbed but not precipitated (Zhou & Li, 2002). Nair *et al.* (1998) reported that originally sorbed P on the solid phase or native P (mg kg⁻¹) can be estimated using a least square fit of P sorbed (x/m) by the solid phase (mg kg⁻¹) vs. equilibrium concentration (C) measured at low P concentration (<10 mg L⁻¹). The linear relationship between P sorbed (x/m) and equilibrium P concentration (C) can be described by, [P sorbed by solid Phase (x/m) = K' C - (P originally sorbed, i.e. native P)], where K' is the linear adsorption coefficient, i.e. slope of the graph (Gale *et al.*, 1994). Originally, sorbed P is Y-intercept, which indicates a negative sign. Villapando (1997) have indicated a good agreement among native sorbed P values estimated by the least square fit method, oxalate extractions, and the anion-impregnated membrane technology.

From above mentioned discussion it can be inferred that a negative sign with Y-intercept shows originally sorbed P (mg kg⁻¹) while a positive (+) sign will point out amount of P adsorbed but not precipitated. It can be inferred that K_f equivalent amount of P will be adsorbed and remaining P may precipitate during the adsorption studies as Zhou and Li (2002) was described.

To test this hypothesis, Freundlich K_f value (mentioned in Table II) were considered as adsorbed P

Table VI. Correlation between the Langmuir and/or the Freundlich equations parameters and soil properties

Correlation between	Regression equation	Correlation coefficient (r)	Coefficient of determination (R ²)
b vs. 1/n	1/n = 0.4848 + 0.0014 (b)	0.921**	0.8491
b vs. K _f	K _f = 0.3746 + 0.0957 (b)	0.898*	0.8070
1/n vs. b	B = -274. + 622.03 (1/n)	0.921**	0.8491
K _f vs. b	b = 31.829 + 8.429 (K _f)	0.898*	0.8070
% OM vs. K _L	% OM = -0.0309 + 0.8476 (K _L)	0.976**	0.9517
% silt vs. K _f	% silt = 4.11 + 1.589 (K _f)	0.927**	0.8601
% silt vs. b	% silt = 21.135 + 0.1927 (b)	0.902**	0.8142
% silt vs. 1/n	% silt = -54.32 + 124.82 (1/n)	0.866*	0.7492
% sand vs. K _f	% sand = 76.346 - 2.1786(K _f)	-0.841*	0.7071

** =Correlation is significant at the 0.01 level (2-tailed).

* =Correlation is significant at the 0.05 level (2-tailed).

Table VII. Comparison between two surface and split plot Langmuir isotherms

Soil #	Two surface Langmuir (TSLI)		Split plot Langmuir (SPLI)		Average (TSLI) R ²
	Region I R ²	Region II R ²	I st Portion R ²	II nd Portion R ²	
1	0.7566	0.9998	0.9553	0.9998	0.8782
2	0.4137	0.9896	0.8204	0.9618	0.7016
3	0.1435	0.9933	0.6113	0.9933	0.5684
4	0.8587	0.9461	0.9534	0.9583	0.9024
5	0.9195	0.9958	0.5971	0.9966	0.9577
6	0.6699	0.1341	0.9828	0.1741	0.4020
7	0.0060	0.9978	0.7141	0.9933	0.5019
Average	0.5382	0.8669	0.8049	0.8617	0.7010

while remaining P [(x/m)-K_f] values were considered as other than adsorbed P (precipitated-P). Langmuir isotherms were constructed separately and named them split Langmuir isotherms. Each split Langmuir isotherm for all seven sodic soils was consisted on two graphs. Ist graph [C/(x/m) vs. C] was constructed up to the K_f value mentioned in Table II. While the IInd graph was constructed between the remaining values [C vs. C/(x/m)] for each soil.

First plot of split Langmuir isotherm. First plot of the split Langmuir isotherm [C/(x/m) vs. C] up to the K_f values, for all the sodic soils proved better than the region I on the individual basis and/or averages (R²) values [(average R² = 0.8049 (split Langmuir Ist) > 0.5382 (Langmuir Region I)]. All the plots were of parabolic shape, which indicated that adsorption decreased with the saturation of sorption sites on the soils under investigation. Parabolic shapes of the curves clearly indicated that in this portion of split Langmuir plot, there was an adsorption process that was being decreased with coverage of the adsorption sites. Rajan and Fox (1975) observed that the P adsorption was associated with an increase in pH and SO₄ release at low level of equilibrium P concentration, while with silicate release throughout P concentration range. They suggested that at low P concentration, P exchange with i) adsorbed SO₄. ii) adsorbed silicate, iii) the water molecules and iv) OH⁻ group

Second plot of split Langmuir isotherm. Second plot of the split Langmuir isotherm [C/(x/m) vs. C] beyond the K_f values, for all the sodic soils under study gave straight lines in all cases with R² values equal to that of two surface Langmuir (Table VII). This may indicate that there was precipitation in this second plot. It can be concluded that at low P concentration up to the Freundlich K_f value, there was P adsorption while beyond this value P precipitation got started in each soil. Cole *et al.* (1953) reported that at high P concentration in the vicinity of fertilizer particles, precipitation of dicalcium phosphate occurred. Based on this it was suggested that nearly all of the P sorbed under these conditions exchange with radioactive P in solution which indicated that P formed monolayer on the CaCO₃ surface.

Soil properties and adsorption parameters. Langmuir adsorption parameters, [i.e. adsorption maximum (b), and bonding energy constant (K_L)] and Freundlich adsorption parameters [(K_f and 1/n)] were correlated with different soil properties like % CaCO₃, % sand, % silt, soluble K⁺, ESP, % organic matter and Cl⁻. It was observed that Langmuir adsorption maximum (b) was significantly correlated with % silt (r = 0.902**). Bonding energy constant (K_L) significantly correlated with % organic matter (r = 0.9760**). While Freundlich 1/n significantly correlated with % sand (r = -0.8410**), % silt (r = 0.8660**), and K_f with % silt (r = 0.9270*). The correlation coefficient values along with linear models are listed in Table VI. Singh and Gilkes (1991) unlike reported that clay contents were major contributors to P sorption in Australian soils. Several researchers have reported positive relationships between the organic matter contents of soils and P sorption (Owusu-Bennoah & Acquaye, 1989; Sanyal & De Datta, 1991). The role of organic matter in increasing the ability of soils to sorb P has been attributed to its association with cations such as Fe, Al and Ca.

CONCLUSIONS

In sodic soils both the Langmuir and the Freundlich model showed comparable validity for prediction. Different adsorption parameters (K_L, b, K_f, and 1/n) significantly correlated with percent sand, silt and organic matter indicating great influence on P adsorption. Split Langmuir isotherms indicated that at low P concentrations (up to the K_f values, i.e. 10.02, 18.05, 16.46, 7.35, 12.42, 29.34, and 30.48 mg P kg⁻¹ for soil 1, 2, 3, 4, 5, 6 and 7, respectively) there may be adsorption of P while beyond this values, there may be P precipitation up to 864.4 mg kg⁻¹. Similarly, the relationship between the percent adsorption as pH and log(x/m) indicated that with each increment of P addition, soils got saturated with P and percent adsorption decreased while pH increased and vice versa. This indicated that during adsorption of P hydroxyl group (OH⁻) was released to affect an increase in pH.

REFERENCES

- Bache, B.W. and E.G. Williams, 1971. A Pphosphate Ssorption Index for Ssoils. *J. Soil Sci.*, 22: 289–91
- Bahl, G.S. and G.S. Toor, 2002. Influence of poultry manure on phosphate availability and the standard phosphate requirement of crop estimated from quantity–intensity relationships in different soils. *Bioresource Tech.*, 85: 317–22
- Bakheit, M.S. and A. Pakermanjie, 1993. Phosphate adsorption and desorption by calcareous soils of Syria. *Commun. Soil Sci. Pl. Anal.*, 24: 197–210
- Barrow, N.J., 1984. Modelling the effect of pH on phosphate sorption by soil. *J. Soil Sci.*, 35: 183–230
- Bouyoucos, G.J., 1962. Hydrometer method improved for making particle size analysis of soils. *Agron. J.*, 54: 464–5
- Bowman, B.T., 1982. Conversion of Freundlich adsorption k values to mole fractions format and the use of Sy values to express relative adsorption of Pesticides. *Soil Sci. Soc. Am. J.*, 46: 740–3
- Castro, B. and J. Torrent, 1998. Phosphorus sorption by calcareous Vertisols and Inceptisols in relation to fertilizer type and soils properties. *Fert. Res.*, 40: 109–19
- Cole, C.V., S.R. Olsen and C.O. Scott, 1953. The nature of phosphate sorption by calcium carbonates. *Soil Sci. Soc. Am. Proc.*, 17: 352–6
- Curtin, D. and R. Naidu, 1998. Fertility Constraints to Pplant Pproduction. In: Sumner, M.E. and R. Naidu (eds.) *Sodic Soils: Distribution, Properties, Management, and Environmental Consequences* (Topic in Sustainable Agronomy). pp. 107–23, Oxford Univ. Press NY, USA
- Curtin, D., F. Selles and H. Steppuhn, 1992a. Influence of salt concentration and sodicity on the solubility of phosphate in soils. *Soil Sci.*, 153: 409–16
- Curtin, D., J.K. Syers and N.S. Bolan, 1992b. Phosphate sorption by soil in relation to exchangeable cation composition and pH. *Australian J. Soil Res.*, 31: 137–49
- Del Bubba, M., C.A. Arias and H. Brix, 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Res.*, 37: 3390–400
- Dominguez, R., C. del. Campillo, F. Pena and A. Delgado, 2001. Effect of soil properties and reclamation practices on phosphorus dynamics in reclaimed calcareous marsh soils from the Guadalquivir Valley, SW, Spain. *Arid Land Res. and Manag.*, 15: 1–19
- Fitter, A.H. and C.D. Sutton, 1975. The use of the Freundlich Isotherm for soil phosphate sorption dData. *J. Soil Sci.*, 26: 241–6
- Gale, P.M., K.R. Reddy and D.A. Graetz, 1994. Phosphorus retention by wetland soils used for treated wastewater disposal. *J. Environ. Qual.*, 23: 370–7
- Graetz, D.A. and V.D. Nair, 1995. Fate of phosphorus in Florida Spodosols–contaminated with cattle manure. *Ecol. Eng.*, 5: 163–81
- Gregory, T., L. Karns Chelsey and Ken D. Shimizu, 2005. A critical examination of the use of the Freundlich isotherm in characterizing molecularly imprinted polymers (MIPS). *Analytica Chemica Acta.*, 528: 107–13
- Griffin, R.A. and J.J. Jurinak, 1973. The Interaction of phosphate with calcite. *Soil Sci. Soc. Am. Proc.*, 37: 847–50
- Gunary, D., 1970. A new adsorption isotherm for phosphate in soil. *J. Soil Sci.*, 21: 72–7
- Harter, R.D. and D.E. Baker, 1977. Application and misapplication of the Langmuir equation to soil adsorption phenomena. *Soil Sci. Soc. Am. J.*, 41: 1077–80
- Hussain, A., A. Ghafoor, M. Anwar–Ul–Haq and M. Nawaz. 2003. Application of the Langmuir and Freundlich equations for P adsorption phenomenon in saline–sodic soils. *Int. J. Agric. Biol.*, 5: 349–56
- Ioannou, A., A. Dimirkou and M. Doula, 1994. Phosphate sorption by cCalcium –bBentonite as describe by commonly used isotherms. *CCommun. Soil Sci. Pl. Anal.*, 25: 2299–312
- John, L.K., 2000. Phosphorus Fractionations. In: *Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters*. Southern cooperative series bulletin No. 396. (Eds.) Gary M. Pierzynski, North Carolina State University, USA
- Kumar, J. and R. Singh, 1998. Phosphorus adsorption and release characteristics of some soils in Ttarai and Bbhabar regions of Utttar Pradesh. *J. Indian Soc. Soil Sci.*, 46: 14–18
- Kuo, S. and E.G. Lotse, 1974. Kinetics of phosphate adsorption and desorption by lake sediments. *Soil Sci. Soc. Am. Proc.*, 38: 50–4
- Moodie, C.D., H.W. Smith and R.A. McCreery, 1959. *Laboratory Manual for Soil Fertility*. pp. 31–9. State college of Washington, Mimeograph, Pullman Washington, D.C., USA
- Muljadi, D., A.M. Posner and A.M. Quirk, 1966. The mechanism of phosphate aAdsorption by Kaolinite, Gibbsite, and Pseudoboemite. I. The Isotherms and the effect of pH on adsorption. *J. Soil Sci.*, 17: 212–29
- Naidu, R. and P. Rengasamy, 1993. Ion interaction and constraints to plant nutrition in Australian sodic soils. *Aust. J. Soil Res.*, 31: 801–19
- Nair, V.D., D.A. Graetz and K.R. Reddy, 1998. Dairy Mmanure Influences on Pphosphorus Rretention Ccapacity of Sspodosols. *J. Environ. Qual.*, 27: 522–7
- Nelson, D.W. and L.E. Sommers, 1986. Total carbon, organic carbon and organic matter. In: Page, A.L., R.H. Miller and D.R. Keeney, (eds.). *Methods of Soil Analysis*. pp. 539–79. Part 2. Agron. 9. SSSA, Madison, WI. USA.
- Owusu–Bennoah, E.O. and D.K. Acquaye, 1989. Phosphate sorption characteristics of selected major Ghanaian soils. *Soil Sci.*, 148: 114–23
- Page, A.L. R.H. Miller and D.R. Keeny, 19828. *Methods of soil analysis*. Part II, ASA, Monograph 9, Madison, W.D., USA.
- Polyzopoulos, N.A., V.Z. Keramidas and H. Kiosse, 1985. Phosphate sorption by some alfisols of Greece as described by commonly used isotherms. *Soil Sci. Soc. Am. J.*, 49: 81–4
- Rajan, S.S.S. and J.H. Watkinson, 1976. Adsorption of selenite and phosphate on an allophane clay. *Soil Sci. Soc. Am. J.*, 40: 51–4
- Rajan, S.S.S. and R.L. Fox, 1975. Phosphate adsorption by soils: II. Reactions in tropical acid soils. *Soil Sci. Soc. Am. Proc.*, 39: 846–51
- Ryden, J.C., J.R. McLaughlin and J.K. Syers, 1977. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. *J. Soil Sci.*, 28: 72–92
- Sanyal, S.K., S.K. De Datta, 1991. Chemistry of phosphorus transformations in soil. *Adv. Soil Sci.*, 16: 1–120
- Singh, B. and R.J. Gilkes, 1991. Phosphorus sorption in relation to soil properties for the major soil types of south–west Australia. *Australian J. Soil Res.*, 29: 602–18
- Singh, R.K., T.G. Sastry, M.B. Sengupta, N.N. Goswami and B.P. Singh, 1991. Phosphate adsorption in salt– affected soils. *J. Indian Soc. Soil Sci.*, 39: 446–51
- Syers, J.K. and Curtin, 1998. Inorganic reactions containing phosphorus cCycling. In: Tiessen, H. (ed.) *Phosphorus Cycles in Terrestrial and Aquatic Ecosystems*. pp. 17–29. SCOPE/UNEP Regional Workshop/: Europe University of Saskatchewan, Saskatoon, Canada.
- Syers, J.K., M.G. Browman, G.W. Smillie and R.B. Corey, 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. *Soil Sci. Soc. Am. Proc.*, 37: 358–63
- Villapando, R.R., 1997. Reactivity of inorganic phosphorus in the spodic horizon. Ph. D. Diss. Univ. of Florida, Gainesville, FL
- Watanabe, F.S. and S.R. Olsen, 1965. Test of an ascorbic acid method for determining P in water and NaHCO₃ extracts from Soil. *Soil Sci. Soc. Am. Proc.*, 29: 677–8
- Zhou, M. and Y. Li., 2001. Phosphorus–sorption characteristics of calcareous soils and limestone from the southern everglades and adjacent farmlands. *Soil Sci. Soc. Am. J.*, 65: 1404–12

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